



TITLE:

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CITATION:

WATANABE, Hiroshi. MEASUREMENT OF ELECTRICAL CONDUCTIVITY OF GRANITE UNDER HIGH PRESSURE. Contributions of the Geophysical Institute, Kyoto University 1972, 12: 177-186

ISSUE DATE:

1972-12

URL:

<http://hdl.handle.net/2433/178610>

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MEASUREMENTS OF ELECTRICAL CONDUCTIVITY OF GRANITE UNDER HIGH PRESSURES

By

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(Received September 6, 1972)

Abstract

The electrical conductivity of dry granite has been studied at 300 to 1500°C and at 6 to 22 Kb by means of a piston cylinder type high pressure apparatus. Investigations have been made in both a non-powdered sample and a powdered sample in order to study inter-crystalline effects.

In a solid state, measurements were made in the three runs: the first heating run, the first cooling run and the second heating run. The activation energies for both samples at pressures up to about 10 Kb decreased in both the first cooling run and the second heating run compared with that in the first heating run, and at pressures more than 10 Kb , the conductivity curves in these three runs for the non-powdered sample agreed well with each other, while the proportionality constant for the powdered sample decreased by a factor of about 10 in both the first cooling run and the second heating run compared with that in the first heating run.

Melting temperatures were determined from the discontinuous changes in the slope of the conductivity curve. The melting temperatures for dry granite increase with pressure and the melting intervals are about 200°C . The increase in the electrical conductivity for the dry granite at the time of melting is about 2 orders of magnitude at high pressures experienced.

In a liquid state, not only the activation energy, E , but also the proportionality constant, σ_0 , increase with pressure in such ways as $\partial E/\partial P = 4.14 \times 10^{-5}\text{ eV/bar}$ and $\partial \log \sigma_0/\partial P = 1.114 \times 10^{-4}\text{ ohm}^{-1}\text{ cm}^{-1}/\text{bar}$.

1. Introduction

A number of data have been obtained on the changes in the electrical conductivity of rocks at the time of melting; for dry basalt, the increase in the electrical conductivity is by a factor of about 10 at atmospheric pressure after Barus and Iddings [1892] and Watanabe [1970], and is about 1 to 2 orders of magnitude at high pressures after Khitarov and Slutskiy [1965], Khitarov *et al.* [1970] and Watanabe [1970], and for dry garnite, the increase in the electrical conductivity is more than 3 orders of magnitude at atmospheric pressure after Levedev and Khitarov [1964], but no data have been obtained at high pressure. Therefore, the author has attempted to determine the increase in the electrical conductivity of dry granite at the time of melting at high pressures.

On the other hand, Kobayashi and Maruyama [1971] concluded from the study of electrical conductivity in single crystals of olivine at atmospheric pressure that the measurement of polycrystalline specimens does not seem to be a reliable way of

learning the properties of electrical conduction. Single crystal samples of silicates in a suitable size for the experiments at high pressures are, however, difficult to obtain. Therefore, it seems very important to study intercrystalline effects at high pressures. The author has also attempted to study the intercrystalline effects on electrical conductivity at high pressures in both a non-powdered sample and a powdered sample.

2. Experimental procedures

The high pressure apparatus used for this study was a single-stage piston cylinder type. The internal arrangement in the high pressure chamber is shown in Fig. 1.

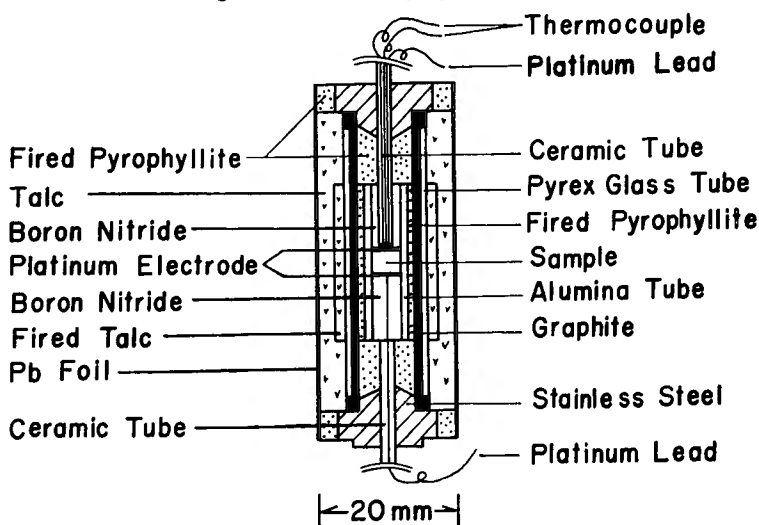


Fig. 1. Internal arrangement in the high pressure chamber.

The experimental apparatus and methods were described in detail elsewhere (Watanabe [1970]). Data were plotted on a load pressure diagram without the friction correction. Temperature was measured with $Pt/Pt-Ph$ 13⁰, thermocouple. No correction was made for the effect of pressure on the *emf* of the thermocouple.

The sample used to determine the electrical conductivity was a natural biotite granite, from Oshima, Oshima-gun, Yamaguchi-prefecture, Japan, of which the chemical composition is given in Table 1. In order to study the intercrystalline

Table 1. Chemical composition of biotite granite used in the present work

SiO ₂	67.94	MnO	tr.	H ₂ O ⁺	0.67
TiO ₂	0.16	MgO	1.46	H ₂ O ⁻	0.12
Al ₂ O ₃	16.00	CaO	4.25	P ₂ O ₅	0.29
Fe ₂ O ₃	1.08	Na ₂ O	2.97	Total	99.97
FeO	2.03	K ₂ O	3.00		

effects on the properties of electrical conduction at high pressures, two kinds of sample were prepared; (a) a non-powdered sample, which was cut in a shape of a cylinder, about 3 mm long and 4 mm in diameter, and was dried at about 900°C for more than 4 hours in nitrogen gas and (b) a powdered sample, which was once sintered in nitrogen gas at about 900°C for more than 4 hours and then crushed as finely as possible.

The sample was inserted into an alumina tube, put between two platinum electrodes, 0.1 mm thick and 4 mm in diameter and fixed by two boron nitride caps. In order to prevent the effects of dehydrated water during the experiment, the boron nitride caps, pyrophyllite rods and tube inside a graphite heater and an inner talc sleeve were previously heat-treated at about 750°C for about 1 hour, and a pyrex glass tube was placed between the graphite heater and the talc sleeves.

After the assemblage was placed in the high pressure chamber, pressure was raised up to about 6 Kb and more and was maintained for more than one night in order to reduce frictions between pressure media.

The electrical conductivity, σ , was calculated from an equation, $\sigma = C/Rx$, where C is a cell constant and Rx is an electrical resistance. The cell constant, C , was calculated from a weight of the sample and a sectional area of the electrodes, which was assumed to be constant during an experiment. The electrical resistance, Rx , was measured by the AC technique at a frequency of 1 KHz.

3. Results and discussion

(1) *On the properties of electrical conduction in a solid state*

Temperatures were raised or lowered by steps at intervals of from 20 to 40°C by manually controlling an electric power. Electrical resistances were measured several times maintaining an experimental temperature at a constant for more than 10 minutes.

(a) *Non-powdered sample*

Results obtained in the non-powdered sample at three different pressures are shown in Fig. 2. Symbols of 'A', 'Ā' and 'B' in Fig. 2 denote the first heating run, the first cooling run and the second heating run, respectively. At about 10.1 Kb (Fig. 2-a), the slope of the conductivity curve, that is, the activation energy decreased remarkably in both the first cooling run and the second heating run compared with that in the first heating run, while the conductivity curves in the three different runs agreed well with each other at about 13.0 Kb (Fig. 2-b) and also at 18.8 Kb (Fig. 2-c).

Changes in the electrical conductivity with time at constant temperatures in the first heating run are also shown in Fig. 2. These results show a slight increase or decrease in conductivity with time, which seems to show that intercrystalline reactions such as sintering do not increase under experimental conditions.

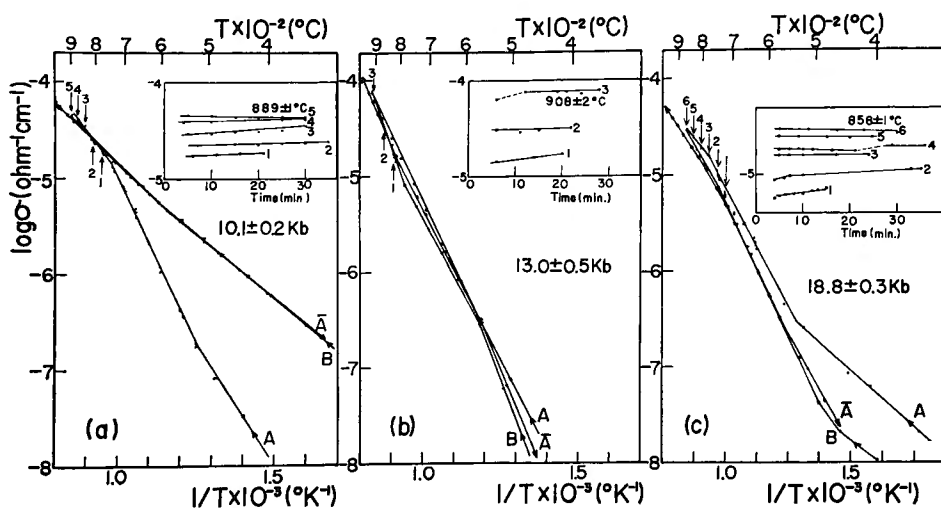


Fig. 2. Variation in conductivity with temperature for the non-powdered granite, (A): first heating run, (\bar{A}): first cooling run, (B): second heating run, (a): 10.1 Kb, (b): 13.0 Kb, (c): 18.8 Kb, and variation in conductivity with time in the first heating run.

(b) *Powdered sample*

Results obtained in the powdered sample at different pressures are shown in Fig. 3. Symbols of 'A', ' \bar{A} ' and 'B' in Fig. 3 denote the first heating run, the first cooling run and the second heating run, respectively. The decrease in the activation energy in both the first cooling run and the second heating run compared with the activation energy in the first heating run was also observed at about 6.75 Kb (Fig. 3-a) and at 6.4 Kb (Fig. 3-b). A quenched sample from the highest temperature experienced did not show any change in mineral composition under examinations by X-ray and optical methods. The changes in conductivity with time are negligibly small at these pressures (Figs. 3-a and 3-b). Therefore, the decrease in the activation energy at lower pressures seems to be quite abrupt not only in the non-powdered sample but also in the powdered sample.

At pressures higher than about 10 Kb, the changes in the electrical conductivity with time were striking (Figs. 3-c, 3-d, 3-e and 3-f). At an intermediate pressure experienced, the changes in the activation energy and the proportionality constant were not so remarkable (Fig. 3-c). But at higher pressures, the proportionality constant decreased by a factor of about 10 in both the first cooling run and the second heating run compared with that in the first heating run, while the activation energy did not change so remarkably in these three runs (Figs. 3-d, 3-e and 3-f).

The quenched sample from the region where such a decrease in conductivity

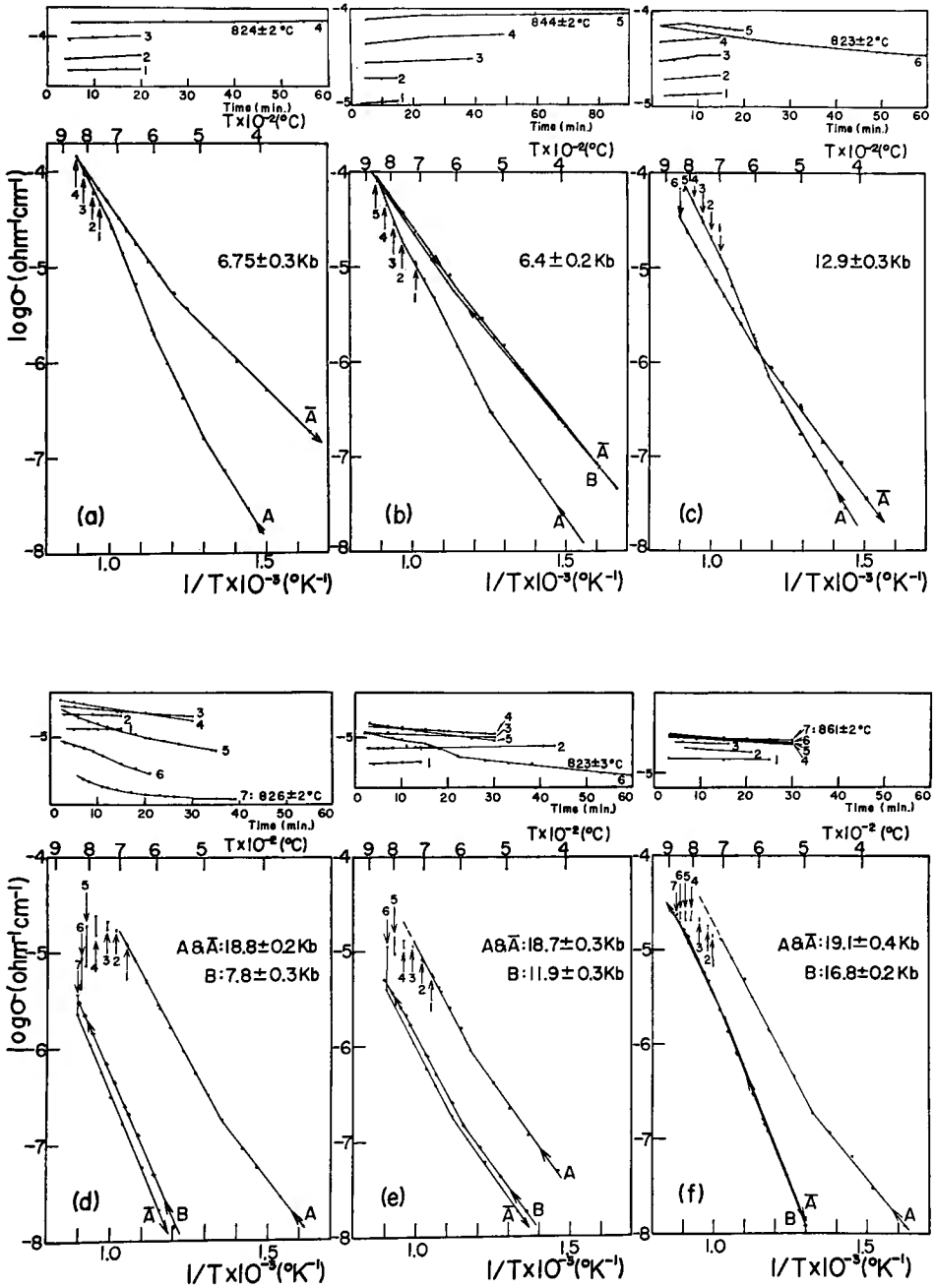


Fig. 3. Variation in conductivity with temperature for the powdered granite, (A): first heating run, (\bar{A}): first cooling run, (B): second heating run, (a): 6.75Kb, (b): 6.4Kb, (c): 12.9Kb, (d): 18.8Kb, (e): 18.7Kb, (f): 19.1Kb, and variation in conductivity with time in the first heating run.

with time was observed did not show any change in the mineral composition under examinations by *X*-ray and optical methods. The temperature at which the linearity of the conductivity curve is broken in the first heating run decreases with pressure. Therefore, the decrease in conductivity with time is due to the intercrystalline reactions such as sintering at high pressure, because the decrease in the diffusion coefficients of conduction ions at the surface of a grain and the grain boundaries as a result of the sintering results in the decrease in the electrical conductivity, as the electrical conductivity, σ , of a conduction ion is connected to the diffusion coefficient, D , in such an equation as $\sigma = (\text{Const.}) \left[\frac{CQ}{kT} \right] D$ (after Brophy *et al.* [1964]), where k is Boltzmann's constant, T is an absolute temperature, and C and Q are the density and the charge, respectively, of the lattice defect connected with a diffusion ion.

Measurements in the second heating run were carried out at a reduced pressure from about 19 Kb in the three samples in order to study the pressure effects on the electrical conductivity. These results, which are also shown in Figs. 3-d, 3-e and 3-f, show a slight decrease with pressure in the proportionality constant and no change in the activation energy.

(2) *On the change of the electrical conductivity at the time of melting*

After the sintering was carried out, temperatures were raised to about 1500°C and then lowered by steps at intervals of 20 to 40°C after maintaining the experimental temperature at a constant for about 10 minutes.

Results obtained in the non-powdered sample at different pressures are shown

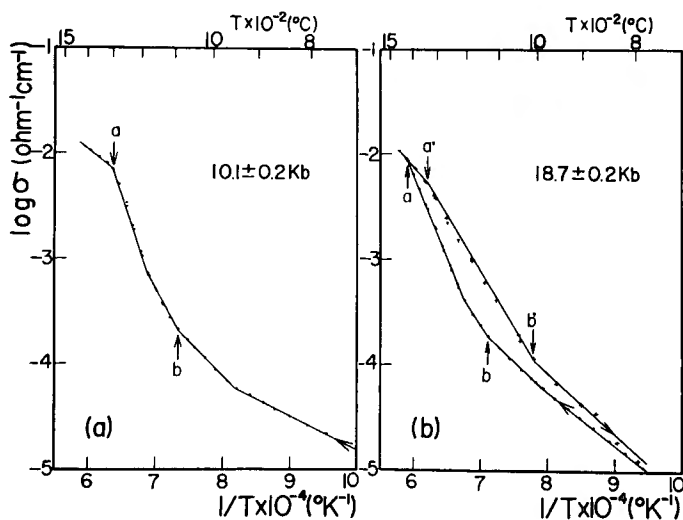


Fig. 4. $\log_{10} \sigma$ versus $1/T$ curve showing discontinuous changes in conductivity for the non-powdered granite at the time of melting, (a): 10.1 Kb, (b): 18.7 Kb. Sections a-b and a'-b' are melting intervals.

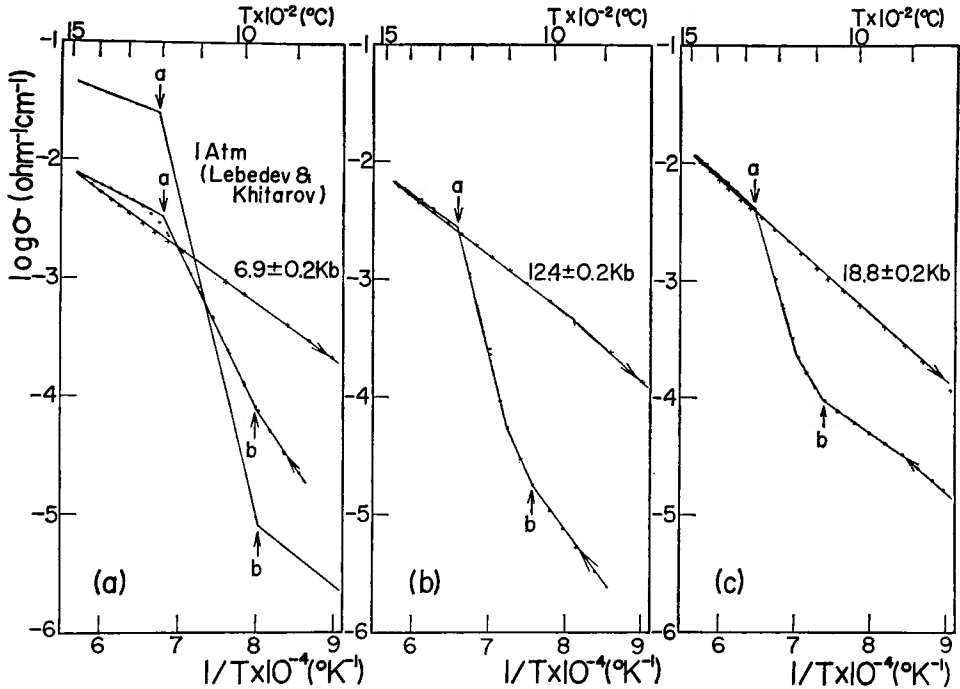


Fig. 5. $\log_{10}\sigma$ versus $1/T$ curve showing discontinuous changes in conductivity for the powdered granite at the time of melting, (a): 6.9 Kb, (b): 12.4 Kb, (c): 18.8 Kb, Section a-b is melting interval.

in Fig. 4 and those in the powdered sample are shown in Fig. 5. The melting temperatures were determined from the discontinuous changes in the slopes of the conductivity curve. Points 'a' and 'b' in Figs. 4 and 5 denote the end of melting and the start, respectively. These results show that the increase in the electrical conductivity at the time of melting is about 2 orders of magnitude in both the non-powdered sample and the powdered sample independent of pressure. This value is about half compared with the result at atmospheric pressure, of more than 3 orders of magnitude, after Levedev and Khitarov [1964], which is also shown in Fig. 5-a.

Quenched melts from the region much above the last break in the conductivity curve showed some relict crystals of quartz under the examination by X-ray method in the non-powdered sample, while those in the powdered sample showed homogeneous melting. These circumstances can easily explain the difference in the conductivity curves in the cooling run between in the non-powdered sample and the powdered sample. The melting temperatures obtained in the non-powdered sample were higher than those in the powdered sample.

Under these circumstances, the melting temperatures of dry granite determined from the data in the powdered sample. These temperatures and those at atmospheric pressure after Levedev and Khitarov [1964] are listed in Table 2 and shown

Table 2. Melting temperatures determined by the electrical conductivity measurements

Pressure, Kb	Solidus temperature, °C	Pressure, Kb	Liquidus temperature, °C
1 atm.*	970	1 atm.*	1250
6.2	991 \pm 2	6.1	1216 \pm 2
6.35	1017	6.4	1211 \pm 3
6.85	977	7.03	1193 \pm 1
8.0	989	8.1	1228 \pm 3
8.9	1002 \pm 2	8.8	1233 \pm 3
12.6	1017	12.5	1235
12.4	1035	12.5	1243
12.5	1017	12.5	1235
15.9	1060	12.6	1225 \pm 6
18.7	1065 \pm 1	18.6	1280 \pm 3
18.8	1071 \pm 3	18.7	1265
18.9	1069	18.8	1271
18.9	1088	19.0	1258
21.9	1101	21.8	1291 \pm 2

* calculated from the data after Levedev and Khitarov [1964].

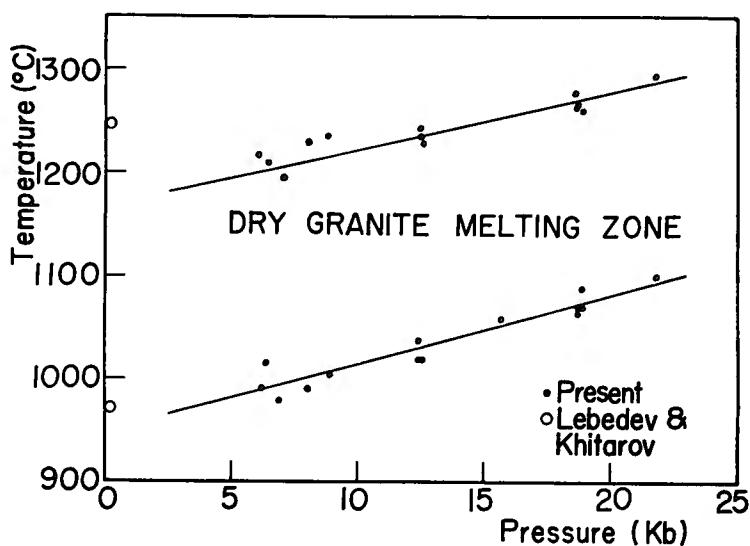


Fig. 6. Melting relations for dry granite determined by electrical conductivity measurements.

in Fig. 6. These results show that the melting temperatures of dry granite increase with pressure and that the melting intervals are about 200°C.

(3) *On the properties of electrical conduction in a liquid state*

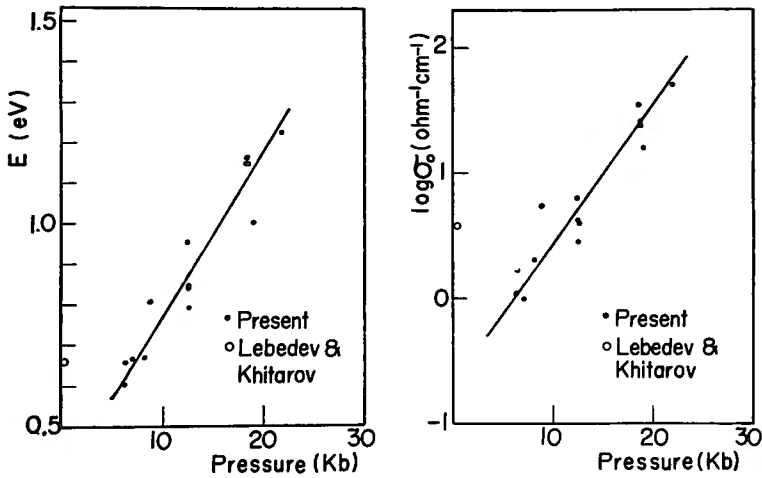
The activation energy, E , and the proportionality constant, σ_0 , in the liquid state were calculated from the data obtained in the powdered sample in the heating run. These values and those calculated from the data after Levedev and Khitarov [1964] are listed in Table 3 and shown in Fig. 7.

These results show that not only the activation energy, E , but also the propor-

Table 3. Variation of E and σ_0 with pressure for molten granite

Pressure, Kb	E , eV	σ_0 , ohm ⁻¹ cm ⁻¹
1 atm.*	0.659	3.781
6.3±0.2	0.615±0.011	1.118±0.104
7.1±0.1	0.669	9.963×10 ⁻¹
8.25±0.15	0.669	2.012
8.85±0.05	0.816	5.527
12.5±0.1	0.844	2.808
12.55±0.05	0.954	4.212
12.6±0.1	0.843	6.300
12.7±0.1	0.792	4.013
18.6±0.1	1.172	3.489×10
18.7±0.1	1.148	2.537×10
18.7±0.1	1.148	2.416×10
19.15±0.15	1.015	1.584×10
21.95±0.15	1.238	5.206×10

* calculated from the data after Lebedev and Khitarov [1964].

Fig. 7. Variation of activation energy (E) and proportionality constant (σ_0) with pressure for molten granite.

tionality constant, σ_0 , in the liquid state increase with pressure in such ways as $\partial E/\partial P = 4.14 \times 10^{-5} \text{ eV/bar}$ and $\partial \log \sigma_0/\partial P = 1.114 \times 10^{-4} \text{ ohm}^{-1}\text{cm}^{-1}/\text{bar}$.

The increase in the activation energy with pressure has been observed for ultramarine in the solid state by Bradley *et al.* [1972]. On the other hand, the activation energy and the proportionality constant of fayalite solid decrease with pressure after Akimoto and Fujisawa [1964] and Bradley *et al.* [1962, 1964]. These situations suggest that the pressure dependences of the activation energy and the proportionality constant are strongly dependent on a conduction mechanism, that is, on the structure of the material. The pressure dependences of the activation

energy and the proportionality constant will be studied in detail in the near future after sufficient data are obtained not only in the solid state but also in the liquid state.

Acknowledgement

The author is indebted to Prof. H. Miki, Prof. S. Matsushima Prof. S. Sasajima, and Mr. M. Shimada of Kyoto University for their valuable advice and encouragement.

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